

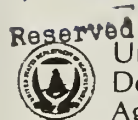
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# Trends in Streamwater Chemistry and Input-Output Balances, Fraser Experimental Forest, Colorado

Robert Stottlemyer and Charles Troendle



### **Abstract**

Precipitation chemistry on the Fraser Experimental Forest is some of the least altered in Colorado. Volume weighted mean pH is 5.32 ( $4.8 \mu\text{eq/l}$ ), nitrate concentration is  $9.7 \mu\text{eq/l}$ , and sulfate  $16.6 \mu\text{eq/l}$ . Calcium and sulfate are the dominant ionic inputs; calcium and bicarbonate are the dominant stream outputs. Calcium and sulfate show a significant ( $p < 0.01$ , Kendall's tau) increase in stream concentration (unweighted) from 1965 to 1984.

### **Acknowledgements**

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**Trends in Streamwater Chemistry and  
Input-Output Balances,  
Fraser Experimental Forest, Colorado**

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# Trends in Streamwater Chemistry and Input-Output Balances, Fraser Experimental Forest, Colorado

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## Introduction

A watershed ecosystem approach increasingly is being used to detect long-term trends in surface water chemistry attributable to land-use, and to estimate the potential effects of human-caused atmospheric inputs. Trends in selected streamwater chemical constituents often can be masked by natural variation in the amount of precipitation. This is because of relationships between precipitation and runoff, and streamwater concentration and yield (Lewis and Grant 1979a, Stottlemeyer 1984). Long-term hydrologic and streamwater chemistry records are needed to determine the amount of natural variation.

However, long-term hydrologic records for watersheds are rare, especially for ecosystems in the western United States. These include data from the 297-ha Fool Creek watershed established in 1940. This was followed in 1943 by the 827-ha East St. Louis watershed, and the 278-ha Deadhorse Creek and 124-ha Lexen Creek watersheds established in 1955, all on the Fraser Experimental Forest.

Similarly, although there is much information available on streamflow chemical composition and yield in general, little of it is for watersheds in Colorado (Baron et al. 1984, Lewis and Grant 1979b). Furthermore, there is considerable variation in geology, vegetation, and proximity to potential urban/industrial pollution sources in the Rocky Mountain region. More baseline data are needed to properly examine ecosystem nutrient conservation mechanisms and their effectiveness following land disturbance and inputs of atmospheric contaminants.

This paper presents inorganic streamwater chemistry data gathered in 1982 and 1984 for Lexen and Deadhorse (main gaging station) watersheds, and compares it to data collected at these sites in 1970–71 by the Forest Service<sup>2</sup> and 1965 (Stottlemeyer and Ralston 1970). The objectives are: (1) to provide a baseline against which future change resulting from atmospheric inputs and watershed manipulation might be measured; (2) to examine historical trends attributable to environmental changes that have taken place since 1965; (3) to examine relationships between precipitation, streamwater discharge, and nutrient concentration; and (4) to compare present precipitation and stream chemistry data at Fraser with other locations in Colorado.

## Study Area

The Fraser Experimental Forest, established in 1937, is approximately 137 km west of Denver, Colo. The coterminous Lexen and Deadhorse watersheds have eastern

aspects. The elevation of Deadhorse varies from 2,863 m at the main gaging station to 3,515 m at the summit of Bottle Mountain. Lexen's gaging station is at 2,985 m, and its upper reach also extends to the top of Bottle Mountain. Deadhorse is a second-order stream, and Lexen is first-order at the gaging stations.

The mean annual precipitation at the Forest Headquarters (elevation 2,725 m) is 58 cm. Precipitation over the entire forest averages 74 cm (Alexander and Watkins 1977). Two-thirds falls as snow. Because of Lexen's slightly higher mean elevation, the long-term precipitation exceeds that of Deadhorse by about 20%.<sup>3</sup> Mean annual runoff from Lexen and Deadhorse during this study was  $50 \pm 11$  and  $35 \pm 7$  cm, respectively.

The bedrock of both watersheds includes some remnants of sedimentary sandstone (Dakota and Morrison formations) at upper elevations. Both watersheds were glaciated, and their headwaters originate below cirques. The streams flow over small terminal moraines composed mostly of fine sands (Retzer 1962). Soils of both watersheds are dominated by gravelly sandy loams with alluvial soils near the streams. The gravelly sandy loams are derived from gneiss and schist parent material that underlines both watersheds beneath the upslope sedimentary sandstones (Troendle 1983). The resistance of this bedrock is one reason for the rugged terrain and the low inherent fertility of the soils. Dominant minerals in the bedrock are quartz and feldspars with metamorphic minerals.

Watershed vegetation along the stream bottoms, northern slopes, and upper elevations consists of Engelmann spruce (*Picea engelmannii*)-subalpine fir (*Abies lasiocarpa*). Lodgepole pine (*Pinus contorta*) dominates all lower and mid-elevation southern aspects, and both watersheds have alpine tundra above timberline (approximately 3,650 m). There is little herbaceous vegetation, except along the streams. The forest floor often is covered with whortle-berry (*Vaccinium* spp.).

## Methods

Streams were sampled just above the gaging station and stilling pond, weekly, from late April to October. Occasionally, they were sampled during winter, when stream discharge was very low and unchanging, to see if stream chemistry also was unchanged. Water samples were collected from the center of the stream, in 500-ml Nalgene polyethylene bottles. The 1965 precipitation and streamflow samples were analyzed only for specific conductance (Industrial Instruments RD-15 Solu Bridge) in

<sup>2</sup>H. Keller and E. Frank, unpublished data, Rocky Mountain Forest and Range Experiment Station, Fort Collins, Colo.

<sup>3</sup>C. A. Troendle, Rocky Mountain Forest and Range Experiment Station, unpublished data.



the field. Unfiltered samples then were refrigerated and later analyzed for calcium, magnesium, sodium, and potassium with a model 303 Perkin-Elmer Atomic Absorption (AA) Spectrophotometer.<sup>4</sup> The 1970–71 samples were analyzed by the Rocky Mountain Forest and Range Experiment Station personnel. Cations were analyzed using atomic absorption procedures, and sulfate was analyzed using the thorin colorimetric method.

Before 1982, pH was not determined, and before 1984, alkalinity was not routinely determined. For pH and alkalinity determinations, samples were brought up to room temperature (APHA 1981) at Station headquarters and all analyses completed within 8 hours after sample collection.<sup>4</sup>

Samples collected since 1982 then were frozen until they were analyzed for other chemical constituents. After filtering (0.45  $\mu$ m), cations and anions were analyzed on an automated Dionex Model 2020 ion chromatograph (IC),<sup>5</sup> and the results were directly fed into a laboratory computer. Silica was determined colorimetrically. Laboratory quality assurance procedures included splitting weekly National Atmospheric Deposition Program (NADP) samples (Station M99), participation in the EPA's National Acid Precipitation Assessment Program (NAPAP) quality assurance (QA) program, routine use of National Bureau of Standards inorganic standards, and the long-term comparison of paired cation results from AA and IC. Early QA results and procedures have been published (Stottlemeyer 1986), and annual QA reports now are prepared.

Precipitation quality was measured weekly at Headquarters using an Aerochem Metrics<sup>4</sup> precipitation collector. This sampler is only open during rain or snow. Samples were processed in the same manner as stream samples. Daily precipitation quantity was recorded with a standard recording rain gauge. Before 1983, precipitation samples were collected in a bulk collector at the same site. To avoid possible anomalous trends attributable to changes in collection procedure, bulk precipitation samples collected in 1982 and early 1983 are not included in table 1. There are no precipitation quality data for the sampling period 1970–71; and the 1965 precipitation chemistry was confined to the analysis of cations.

Input/output budgets for dissolved inorganics were computed for the watersheds as follows. For the 1984 precipitation data, there was not a significant correlation between precipitation ionic concentrations and precipitation amount. Therefore, ionic input was calculated using the mean unweighted ionic concentrations ( $\mu$ eq/l) times the total amount (wet-only in cm) of precipitation that fell and converting to eq/ha. This value was corrected for the elevation increase in precipitation that falls in each watershed. Because precipitation samples for

chemical analysis were not collected right in the watersheds, no correction was made for possible variation in precipitation quality with elevation (Lewis et al. 1984). Except for the years 1965 and 1984, when precipitation chemistry was determined, input values were estimated from the precipitation chemistry data collected in 1984 weighted by the amount of precipitation that fell in 1970, 1971, and 1982. This assumes that precipitation chemistry during those years did not differ significantly in concentration. This seems reasonable for this region (NADP 1985, Oppenheimer et al. 1985). If precipitation was lower in ionic concentration, then these output values would be conservative.

Weekly dissolved ion output in streamflow, which is principally a measure of soil weathering, exchangeable ions, biological activity, and organic decomposition, was estimated as follows. For cations, which have a good linear relationship to discharge, weekly output was determined by taking the mean concentration between successive weekly samples multiplied by the streamwater discharge for the week, which was calculated from mean daily discharge. For anions, which did not have a good relationship of concentration to discharge, annual output was computed by taking the annual mean unweighted concentration times the total streamwater discharge for the year.

The calculations assume that the watersheds have little or no deep seepage. Long-term annual streamwater discharge from these watersheds was 50% of annual precipitation input. Summer interception of precipitation by lodgepole pine approached 25% to more than 60% for Engelmann spruce and subalpine fir (Stottlemeyer and Ralston 1970). Canopy interception of incident snowfall by these species could approach similar values, depending on local conditions. These values, which do not include estimates of sublimation and forest floor evaporation, suggest there is little opportunity for deep seepage from these watersheds. Further evidence is provided by the absence of faulting nearby, and the fact the entire watersheds are underlined with schist and gneiss bedrock.

## Results

Calcium was the dominant cation and sulfate was the dominant anion in 1984 incident precipitation (wetfall only) (table 1). The concentrations of chemical species with possible human origin, principally hydrogen ion, ammonium, nitrate, and sulfate, appear to be some of the lowest in the State.

The precipitation amount in 1984 was 45% greater than the long-term average of 58 cm (table 2). The inputs (eq/ha/yr) of all cations was somewhat more than observed at most other NADP stations in Colorado. In a year with average precipitation, calcium and magnesium inputs at Fraser could be similar to the other stations, while the inputs of sodium and potassium might be higher. In 1984, inputs of chemical species with possible human origins were similar to other stations, except for hydrogen, which was somewhat lower, and sulfate, which was somewhat higher. Comparing Fraser data to NADP

<sup>4</sup>The 1965 samples were analyzed at the Department of Geology, Duke University, Durham, North Carolina. Since 1982, pH has been determined at Station headquarters using a Fisher AC meter, and alkalinity determined by titration with 0.02N H<sub>2</sub>SO<sub>4</sub> to pH 4.5 endpoint. Anions and cations are analyzed at the Department of Biological Sciences, Michigan Technological University, Houghton, Mich. Precipitation collector at Headquarters is wet/dry collector by Aerochem Metrics, Bushnell, Fla.

<sup>5</sup>Use of trade names does not, in any manner, constitute endorsement by the U.S. Forest Service.



data from an eastern site (Hubbard Brook, New Hampshire) receiving large amounts of human inputs allows some comparisons of human inputs to Fraser and other stations in Colorado (table 2). Correcting for differences in precipitation amount, it appears that, except for potassium, ecosystem inputs at this eastern site are many orders of magnitude greater than those observed in Colorado, especially for chemical species of human origin (Likens et al. 1977).

Even though streamwater discharge may vary more than 25-fold annually (fig. 1), streamwater concentrations (unweighted) of most dissolved substances vary within a relatively narrow range, generally less than a factor of three (figs. 2, 3, 4). The exception to this is nitrate (fig. 4), which also can vary about 25-fold annually. This probably was the result of watershed disturbance caused by installation of upstream gaging stations during 1970 and 1971 in Deadhorse. The lowest ionic concentrations were observed during the second half of June, during peak snowpack runoff. The highest values were from late July to October. Chloride (1984), nitrate, ammonium (1984), and potassium all were diluted more than threefold during high spring streamflow. Calcium, magnesium, and sodium were diluted about twofold, and sulfate less than twofold during high stream discharge. Complete alkalinity data are available only for 1985; and both streams were well buffered (volume weighted bicarbonate alkalinity for Lexen = 715  $\mu\text{eq}$ , Deadhorse = 1,000  $\mu\text{eq}$ ).

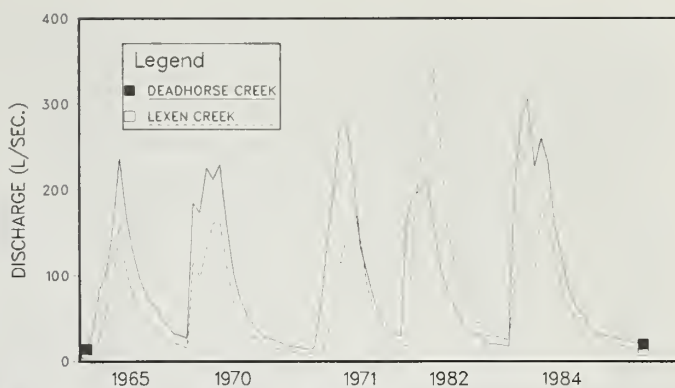


Figure 1.—Stream discharge (l/sec) from Deadhorse and Lexen Creeks from May to September for years indicated.

Calcium and sulfate showed a significant ( $p < 0.01$ , Kendall's tau) increasing trend in unweighted stream concentration (figs. 2, 4) from 1965 to 1984, but there was no significant trend for other ions, streamwater discharge, or precipitation. Use of this nonparametric test on seasonally variable data was described by Hirsch et al. (1982).

A summary of Deadhorse and Lexen streamwater chemistry from 1965 to 1984 shows volume weighted mean annual concentrations of calcium and sulfate increased in recent years (table 3); but the number of years was too few to detect any possible significant trends.

Table 1.—Weighted average ion concentration ( $\mu\text{eq/l}$ ) of 1984 incident precipitation at Fraser Experimental Forest, and 1982 data for selected NADP stations in Colorado and Hubbard Brook, New Hampshire. Standard deviation is in parentheses.

Ion	Fraser	Mesa Verde	Sand Spring	Manitou	Rocky Mountain	Hubbard Brook
Ca	17.6(16.2)	16.5	13.5	10.5	10.5	4.0
Mg	2.7( 2.6)	3.0	3.5	3.2	3.0	2.1
Na	9.6(10.1)	0.8	1.0	3.0	2.1	3.8
K	7.6( 6.5)	1.3	2.0	1.4	1.4	0.4
NH <sub>4</sub>	5.1( 4.6)	7.2	8.9	9.4	7.7	10.0
H	4.8( 2.8)	20.4	9.3	12.3	10.7	45.7
NO <sub>3</sub>	9.7( 5.6)	14.3	12.9	18.2	15.0	25.0
SO <sub>4</sub>	16.6(13.6)	29.8	19.8	21.2	18.9	41.4
Cl	11.2( 7.1)	2.5	2.8	3.1	2.5	4.2

Table 2.—Ionic inputs (eq/ha/yr) during 1984 at Fraser Experimental Forest and during 1982 for selected NADP stations in Colorado and at Hubbard Brook, New Hampshire. Standard deviation is in parentheses.

Ion	Fraser	Mesa Verde	Sand Spring	Manitou	Rocky Mountain	Hubbard Brook
Ca	181(209)	107	51	48	39	410
Mg	27( 26)	19	13	15	11	210
Na	81( 98)	5	4	14	8	390
K	64( 63)	8	7	6	5	40
NH <sub>4</sub>	43( 44)	47	33	43	28	1020
H	40( 25)	132	35	56	39	4640
NO <sub>3</sub>	104( 64)	93	48	83	55	2540
SO <sub>4</sub>	186(138)	193	74	97	70	4210
Cl	97( 63)	16	10	14	9	430
cms <sup>1</sup>	84	65	37	46	37	102

<sup>1</sup>Centimeters of precipitation.

Volume weighted mean annual concentrations of all cations, except for potassium, in these streams appear much higher than observed in other Fraser Experimental Forest watersheds or nearby Rocky Mountain watersheds (table 4). Concentrations of ammonium and nitrate were lower, while concentrations of sulfate were much higher.

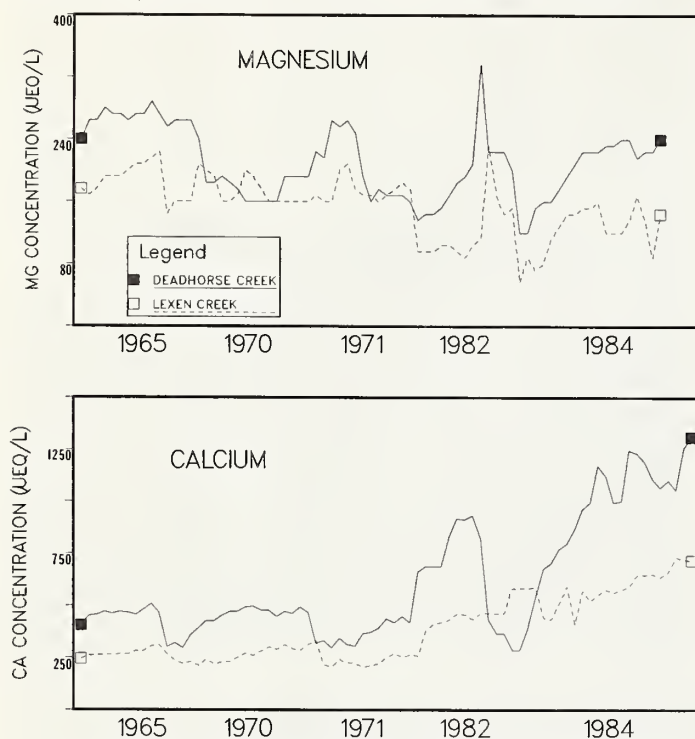


Figure 2.—Time trend of Mg and Ca concentration ( $\mu\text{eq/l}$ ) for Deadhorse and Lexen Creeks for the period of study.

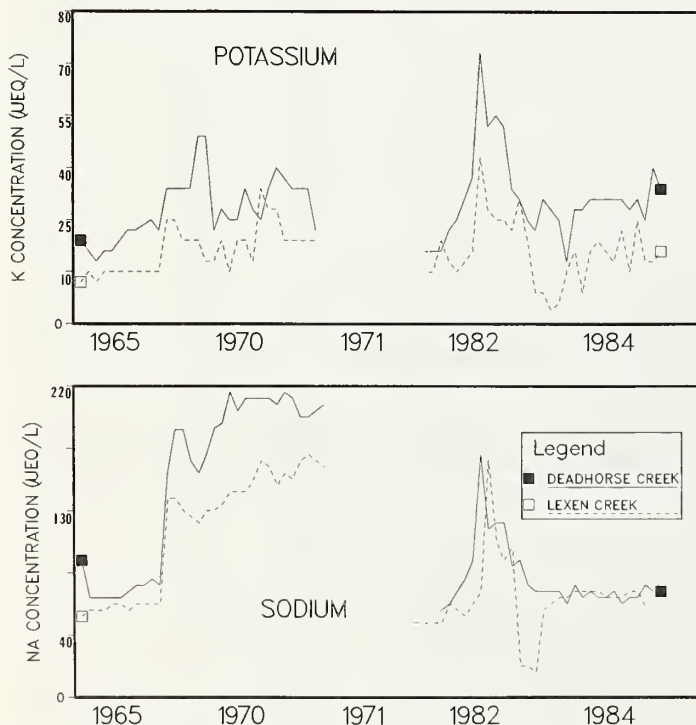


Figure 3.—Concentrations of K and Na ( $\mu\text{eq/l}$ ) for Deadhorse and Lexen Creeks for the period of study.

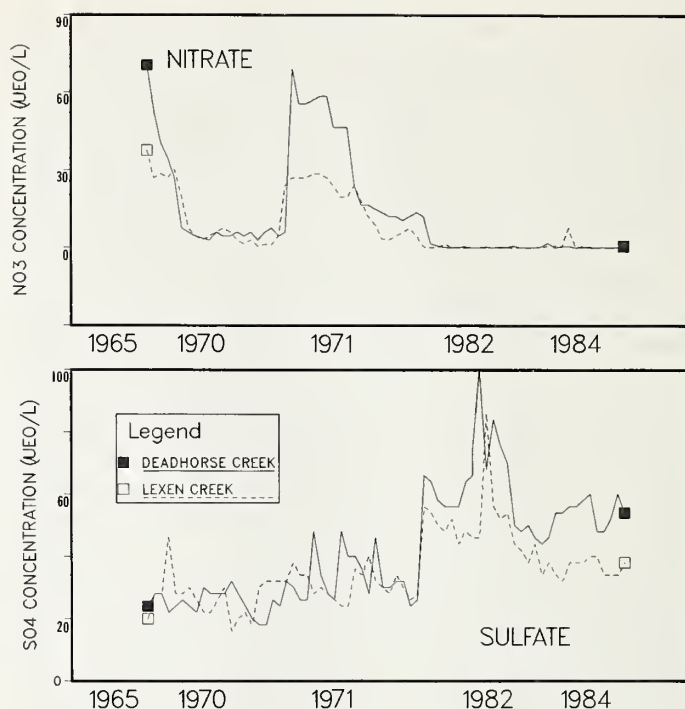


Figure 4.— $\text{NO}_3$  and  $\text{SO}_4$  concentrations ( $\mu\text{eq/l}$ ) for Deadhorse and Lexen Creeks for the period of study.

Simple linear regression models of stream concentration (dependent variable) and instantaneous discharge (independent variable) for each year show most cation concentrations significantly correlated with stream discharge (table 5). Calcium, magnesium, sodium, and potassium generally showed a significant inverse relationship to streamwater discharge, while ammonium, chloride, nitrate, and sulfate showed no significant trend with streamwater discharge (table 5).

Calcium made up about 78% of the dissolved cation loss from Deadhorse and 80% of the total dissolved cation loss from Lexen (table 6). Total stream cation export appeared to exceed total anion output (table 3). However, silicate and bicarbonate alkalinity data collected in 1985, the first full year of data for these species, indicate that these are dominant anions in these watersheds and account for most of the anion deficiency seen in table 3. Thus, the concentration of organic acids, while not directly determined, would appear to be very low in these streams.

Most cations showed net losses from the watersheds relative to precipitation inputs (table 6). Potassium showed the least export relative to precipitation inputs, especially during 1982 and 1984. Ammonium, nitrate, and hydrogen ion were retained in the ecosystems. Sulfate outputs also exceeded precipitation inputs. Sulfate ion loss appeared to be relatively greater in Lexen. There was a definite trend of increasing sulfate discharge from Deadhorse; but this does not reflect the estimated precipitation inputs, except for 1984.

Because the dissolved solids concentrations were relatively constant in streamwater, especially the cations, the gross output of most major ions should have been related to annual streamflow and somewhat predictable. There appears to be a rough linear relationship between



Table 3.—Volume-weighted average annual streamwater chemistry concentrations ( $\mu\text{eq/l}$ ) for Deadhorse and Lexen Creeks, Fraser Experimental Forest. Standard deviation is in parentheses.

Ion	1965		1970		1971		1982		1984	
	D	L	D	L	D	L	D	L	D	L
Calcium	447(29)	262(15)	377(67)	237(25)	322(34)	224(18)	729(139)	449(52)	880(192)	531(87)
Magnesium	267(19)	190(17)	235(38)	177(23)	258(34)	144(44)	163( 35)	129(50)	172( 40)	98(31)
Sodium	78( 12)	61( 3)	179(18)	135(10)	—	—	66( 20)	79(40)	69( 7)	44(22)
Potassium	20( 3)	12( 1)	34( 8)	20( 4)	—	—	23( 9)	20( 9)	28( 6)	13( 9)
Ammonium	—	—	—	—	—	—	—	—	0.3(0.6)	2( 2)
Nitrate	—	—	32(24)	23(13)	52(19)	20( 9)	0.4( 0.4)	0.2(0.5)	1( 1)	0.3( 1)
Sulfate	—	—	26( 3)	28( 3)	36( 9)	32( 3)	64( 8)	58(14)	52( 4)	39( 4)
Flow <sup>1</sup>	86	55	86	54	185	75	85	64	115	66

<sup>1</sup>Mean instantaneous flow (l/sec) at the time of stream sampling.

Table 4.—Volume-weighted average annual streamwater chemistry concentrations ( $\mu\text{eq/l}$ ), Fool and East St. Louis Creeks in Fraser Experimental Forest, Como Creek at Niwot Ridge, and Loch Vale, Rocky Mountain National Forest.<sup>1</sup> Standard deviation is in parentheses.

Ion	Fool	St. Louis	Como	Loch Vale
Ca	297.00(50.2)	223.20(34.0)	92.30	66.1
Mg	84.60(16.8)	63.00(12.7)	43.60	19.6
Na	83.80(10.1)	68.30(18.7)	55.70	18.9
K	32.00(10.8)	26.20(15.5)	6.60	6.4
NH <sub>4</sub>	0.98( 1.5)	0.40( 0.7)	0.60	4.2
H	0.14( 0.1)	0.12(0.04)	0.15	10.7
NO <sub>3</sub>	0.11(0.23)	2.80( 1.0)	0.06	20.5
SO <sub>4</sub>	37.80( 3.0)	38.90( 7.0)	7.90	32.6
Cl	18.80(12.1)	19.00(15.8)	—	5.9
PO <sub>4</sub>	0.23( 0.7)	0.04( 0.5)	0.12	—
HCO <sub>3</sub>	—	—	181.90	46.3

<sup>1</sup>Rocky Mountain National Park data for 1984 provided by Jill Baron, Colorado State University. Fraser Experimental Forest data from 1984. Como Creek data from 1975-78 (taken from Lewis and Grant 1979b).

Table 5.—Results of F test for regression of ionic concentration and stream discharge, Deadhorse and Lexen Creeks, Fraser Experimental Forest.<sup>1</sup>

Ion	Deadhorse					Lexen				
	65	70	71	82	84	65	70	71	82	84
Ca	-.86	-.89	-.82	ns	-.84	-.74	-.73	-.55	-.53	-.82
Mg	-.81	.76	.81	-.77	-.92	-.81	ns	.55	-.33	-.94
Na	ns	-.45	—	-.81	ns	-.90	-.85	—	-.40	-.89
K	-.65	.88	—	-.82	ns	ns	ns	—	-.32	ns
NO <sub>3</sub>	—	—	—	ns	ns	—	—	—	ns	ns
SO <sub>4</sub>	—	ns	ns	.47	.53	—	ns	ns	ns	ns

<sup>1</sup>Where F test is significant, R values are given.

annual streamflow and total cations (fig. 5), except perhaps for 1984, a year when precipitation input at Fraser headquarters exceeded the long-term average by almost 45%. Sulfate, the only anion measured over four of the five sampling years, showed no such trend.

## Discussion

### Precipitation

Precipitation at the Fraser Experimental Forest appears to be some of the cleanest in the State. In addition to the NADP data comparisons, data collected by Lewis et al.

(1984) in 1982-83 from a more intensive 42-station network in Colorado showed only two sites, Wolf Creek Pass and Wray, had lower average sulfate levels. Only one station, Wolf Creek, had lower nitrate concentrations. However, a qualifier in this comparison is Lewis et al.'s (1984) use of specially designed bulk collectors rather than event collectors. The latter have much less dry deposition included in the sample, a significant qualifier for calcium, potassium, sulfate, and nitrate. This also could help explain why only three of their stations, Wolf Creek, Rabbit Ears, and Dillon, had slightly lower total cation concentrations. This group includes two of the highest elevation stations in their network.

Table 6.—Annual input/output budgets and net export (eq/ha) for major ion species, Deadhorse and Lexen Creeks, Fraser Experimental Forest. Standard deviation is in parentheses.

Ion	1965		1970		1971		1982		1984	
	D	L	D	L	D	L	D	L	D	L
Calcium										
Input	125	150	138	166	133	159	135	162	181(209)	223(281)
Output	1851(41)	1362(60)	1542(123)	1342(142)	933(83)	1282(116)	1968(452)	1482(192)	3960(491)	3027(309)
Net	-1726	-1212	-1404	-1176	-800	-1140	-1833	-1320	-3779	-2804
Magnesium										
Input	18	22	20	24	19	23	19	25	26( 26)	32( 31)
Output	1102(29)	1004(54)	954(104)	1012(108)	742(82)	819( 62)	443(113)	426(171)	774( 75)	559( 68)
Net	-1084	- 982	- 934	- 988	-723	- 796	- 424	- 401	- 748	- 527
Sodium										
Input	70	84	77	93	72	87	74	88	102(123)	148(178)
Output	265(56)	274( 6)	734( 38)	770( 43)	—	—	178( 61)	261(130)	310( 23)	251( 53)
Net	- 195	- 190	- 657	- 677	—	—	- 104	- 173	- 208	- 103
Potassium										
Input	55	67	61	73	57	69	58	70	80( 79)	96( 96)
Output	68( 9)	54( 3)	139(25)	114( 29)	—	—	62( 26)	66( 32)	126( 21)	74( 43)
Net	- 13	13	- 78	- 41	—	—	- 4	4	- 46	22
Ammonium										
Input	37	45	41	50	39	47	39	47	54( 55)	77( 80)
Output	—	—	—	—	—	—	—	—	<2	<2
Net	—	—	—	—	—	—	—	—	52	75
Nitrate										
Input	71	85	79	95	74	89	75	90	103( 64)	124( 77)
Output	—	—	68( 87)	68( 75)	128(69)	86( 57)	1( 1)	1( 6)	4( 4)	2( 10)
Net	—	—	11	27	- 54	3	74	89	99	122
Sulfate										
Input	128	154	142	170	133	160	135	162	186(138)	233(165)
Output	—	—	106( 17)	149( 27)	100(23)	185( 22)	198( 42)	195( 42)	249( 25)	224( 21)
Net	—	—	36	21	33	- 25	- 63	- 33	- 63	- 1
Pr/Sr <sup>1</sup>	58/34/45		64/41/57		60/29/58		61/27/33		84/45/57	

<sup>1</sup>Precipitation at headquarters and stream discharge for Deadhorse and Lexen Creeks in cms. Inputs corrected for elevation differences between headquarters, Deadhorse and Lexen watersheds.

The Fraser site may benefit from its relatively high elevation and its location just west of the Continental Divide, which decreases the probability of invading air contaminants from the Denver metropolitan area. But, it could be subject to human inputs from the Southwest (Oppenheimer et al. 1985). Regardless, the present evidence suggests that Fraser has had relatively little human-caused atmospheric inputs, compared to other sites in the region.

Lewis et al. (1984) suggest that precipitation at lower elevation sites in Colorado is richer in calcium and magnesium. Higher elevation sites, because of differences in transport mechanisms, should be relatively richer in anions from strong acids. At Fraser, the ratio of  $\text{Ca} + \text{Mg} / \text{NO}_3 + \text{SO}_4$  is 0.59 for 1984 precipitation data. This value is very similar to the 0.64 Lewis et al. (1984) found at Frisco (elevation 2,770 m), but is higher than the 0.35 observed by Lewis et al. (1984) at Dillon (elevation 2,770 m). The Fraser data appear to support the hypothesis of Lewis et al. (1984) that air masses moving over the mountains of Colorado show an increasing bias toward acidifying substances with gain in elevation. Because the Dillon and Frisco sites, 35 km to the southwest across the Williams Fork Mountains, also are just west of the Continental Divide and at the same elevation as Fraser, it appears possible that Dillon is being influenced by local input sources.

## Surface Water

There are suggested unit-area differences in the net export of major ions from the two watersheds (table 6); but with only estimates of precipitation inputs for earlier years (no weekly precipitation chemistry for 1970–71, 1982), the computation of error terms on inputs can not be done. The dissolved ion concentration in Deadhorse streamwater was about 70% greater than for Lexen (table

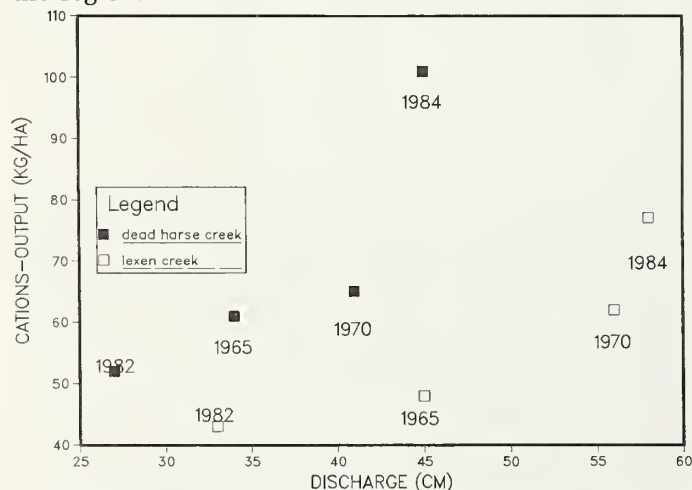


Figure 5.—Relationship between annual streamflow (cm) and output (kg/ha) of cations during 1965–1984. (Cation data for 1971 is incomplete and not presented.)



3), a result which may reflect, in part, the fact that the Deadhorse drainage is more than twice as large as Lexen. Also, Deadhorse Creek is a second-order stream at the lowest station, while Lexen is first-order. In addition, portions of the Deadhorse drainage have been disturbed by installation of additional access roads and gaging stations beginning in 1970, and subsequent small plot cutting beginning in 1978. Average exports from Deadhorse exceed Lexen by about 30%. These differences appear most pronounced and consistent in the 1982–84 data (table 6). However, this question of site alteration and nutrient release is the subject of additional ongoing study. Troendle (1983) found that the cutting, which was 36% of the area in the 41-ha North Fork of Deadhorse, increased water yield from this small drainage. Because the disturbed area is quite small (5.3%) relative to total watershed area, this does not appear to account for the increases noted in table 6.

A better explanation for the suggested increase in ionic discharge from Deadhorse relative to Lexen in recent years probably has more to do with the fact that, of the five years of study, 1984 was the year of highest total precipitation and discharge from Deadhorse (table 6). The concentration of most cations was significantly correlated to discharge (table 5); but the negative slope of regression for Deadhorse is not steep. Thus, net export from Deadhorse, especially calcium, was very high during years of high total discharge relative to Lexen (table 6).

The weighted average ion concentration (table 3) for Deadhorse and Lexen Creeks was considerably higher than recorded at Como Creek (Lewis and Grant 1979b) near Niwot Ridge and for Loch Vale in Rocky Mountain National Park (Baron et al. 1984). The Fraser streams, in addition to receiving relatively clean precipitation, also were well buffered.

The correlations observed between specific ion concentrations and stream discharge (table 5) very closely follow those observed at Como Creek (Lewis and Grant 1979a). However, in almost all cases, the negative regression slopes are less than observed at Como Creek. The relatively poor relationships seen in 1982 at both streams and especially Deadhorse are not readily explained. On all laboratory analyses, we routinely use scatter plots of ion concentration (dependent) and specific conductance (independent variable) to check outliers. In this check, the 1982 data set does not appear much different than other years.

### Input/Output Budgets

Calcium is the major cation lost from these ecosystems. The amount of net loss for this ion varies considerably from year to year. There is no other long-term record to compare with in Colorado. However, the orders of magnitude in change are very similar to those observed in the long-term record at Hubbard Brook, although the net loss of calcium there averages about one-third that observed at Fraser. The magnitude of change observed for the other cation species is similar to calcium. However, the direction of change is less clear. Net loss of magnesium appeared to decline for both watersheds,

while sodium and potassium showed no trend. All cations showed a net loss during the sampling period; however, potassium clearly was the most conserved relative to inputs.

Ammonium has not been analyzed long enough to detect trends, except that it is retained in the watersheds. Hydrogen ion data are not included in table 6, because pH has only been recorded in recent years. In 1984, the mean hydrogen ion concentration in Deadhorse was  $0.11 \mu\text{eq/l}$  ( $\text{pH} = 6.96$ ) and in Lexen was  $0.135 \mu\text{eq/l}$  ( $\text{pH} = 6.87$ ). Thus, it appears that at least 96% of the hydrogen ion input is retained in these watersheds.

Except for sulfate, anion data sets were incomplete until the recent sampling (table 6). Very little nitrate leaves the systems, with net retention exceeding 95% of input. For sulfate, there appears to be a trend toward increasing net loss from the systems, especially from Deadhorse. This trend appears to be primarily related to total stream-water discharge (fig. 1), but also reflects increased stream concentrations of sulfate (fig. 4). Silica data were collected during 1970–71, 1982, and 1984. Its mean concentration in Deadhorse was  $255 \mu\text{eq/l}$  and in Lexen  $246 \mu\text{eq/l}$ . Based on this limited recent data, it appears that bicarbonate and silicate are by far the most important anion species in Lexen and Deadhorse.

The apparent linear relationship between total cation output and annual streamflow (fig. 5) is potentially important. Because chemical concentration of most cations is relatively uniform, the annual output of most cations is directly related to stream discharge. Thus, total cation output is highly predictable. This appears to be true for three (1965, 1970, 1982) of the five years in this study (no monovalent cation stream data exist for 1971). In 1984, this predictability seems to have broken down, particularly for Deadhorse. That year, cation output exceeded that predicted from previous stream discharge data by about 45%. The Deadhorse drainage was disturbed by small plot cutting in the early 1970s. The 1982 gross output data suggest that there was little effect of this disturbance on ecosystem cation loss during a year of low total stream discharge. The 1984 data suggest that during a year of high stream discharge, a threshold was reached where the relationship of total cation output to stream discharge changed. More years' data are necessary to better estimate this trend and assess its significance. However, if it holds, it suggests that the moderately disturbed forest ecosystem can regulate streamwater chemical concentrations over a reasonable range of streamwater discharge.

There are important qualifiers to consider in the present data set. Without more detailed soils data or lysimeter data, not too much can be stated about the relative contributions made by weathering (Waring and Schlesinger 1985). The high levels of bicarbonate in streamwater outputs from these two watersheds suggests much weathering occurs, especially of sedimentary rock and possibly even primary silicate minerals that contain potassium. The relatively high levels of calcium and potassium reflect fast-weathering carbonates, such as from sedimentary rock, rather than weathering of the more resistant primary silicate minerals within the crystalline metamorphosed bedrock underlying the entire watersheds. The



Fraser streamwater chemistry is a composite coming from both primary and secondary mineral sources, which should be distinguished carefully when interpreting geochemical data.

Another qualifier is the lack of intensive sampling during the rise and fall of the annual spring runoff. This also limits the data sets' value in determining the mechanisms that might underlie observed fluctuations (Bond 1979). Also, it qualifies somewhat the time-trends observed in the data thus far. The absence of site-specific data on diurnal variation could be another limitation. However, diurnal variation was monitored at Fool Creek in August 1965, and total cation concentration varied less than 6% (Stottlemeyer unpublished data).

Streamwater quality is a composite of rainwater and groundwater. Groundwater quality can be considerably influenced by its residence time, which is much influenced by topography and presence of soil macropores. Therefore, direct comparisons of these results with those of Knight et al. (1985) are not valid without additional data from Fraser, particularly canopy throughfall and soil lysimeter data. Better assessment of the rate of chemical weathering requires assessing the chemical composition of the soil parent material, also. These data should allow estimation of steady-state chemical weathering for these watersheds, and assessment of possible retention of released ions by clays and other ion exchange sites.

### Conclusions

Present wet-only precipitation quality at the Fraser Experimental Forest appears, on the average, to be some of the cleanest in Colorado.

Major cation and bicarbonate concentrations in Deadhorse and Lexen are much greater than those observed for other Fraser watersheds, or at nearby Niwot Ridge and portions of Rocky Mountain National Park. This largely reflects the different bedrock characteristics of upper portions of these two Fraser watersheds. Caution is required when making generalizations about "representative" ecosystems, their functioning and response to human impact.

Over the period of study, there was a significant inverse linear relation between most cation concentrations and streamflow discharge. These results are in general agreement with findings at Niwot Ridge (Lewis and Grant 1979a) and in Red Butte Canyon in Utah (Bond 1979). However, the slope of this regression is low, suggesting that ecosystem conservation mechanisms are not as well developed as those at other sites. This is especially true during periods of high discharge. There are no significant correlations between anion concentration and streamwater discharge.

Time trends in net watershed ion export appear to be present for calcium and sulfate, both of which are increasing, and for magnesium, which is decreasing. There is considerable yearly variation in streamwater ion concentration, but not unlike the magnitude found at other sites, such as Hubbard Brook, New Hampshire.

The apparent predictability of outputs of dissolved substances in streamflow based upon hydrologic outputs

is important. This could provide a valuable baseline for measuring change that might result from human sources. The Fraser data point out the considerable differences in streamwater chemistry present in Rocky Mountain watersheds that are nearby.

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Precipitation chemistry on the Fraser Experimental Forest is some of the least altered in Colorado. Volume weighted mean pH is 5.32 (4.8  $\mu\text{eq/l}$ ), nitrate concentration is 9.7  $\mu\text{eq/l}$ , and sulfate 16.6  $\mu\text{eq/l}$ . Calcium and sulfate are the dominant ionic inputs; calcium and bicarbonate are the dominant stream outputs. Calcium and sulfate show a significant ( $p < 0.01$ , Kendall's tau) increase in stream concentration (unweighted) from 1965 to 1984.

**Keywords:** Precipitation chemistry, water quality, subalpine hydrology

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Rocky  
Mountains



Southwest



Great  
Plains

U.S. Department of Agriculture  
Forest Service

## Rocky Mountain Forest and Range Experiment Station

The Rocky Mountain Station is one of eight regional experiment stations, plus the Forest Products Laboratory and the Washington Office Staff, that make up the Forest Service research organization.

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Research programs at the Rocky Mountain Station are coordinated with area universities and with other institutions. Many studies are conducted on a cooperative basis to accelerate solutions to problems involving range, water, wildlife and fish habitat, human and community development, timber, recreation, protection, and multiresource evaluation.

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Flagstaff, Arizona  
Fort Collins, Colorado \*  
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